

COATINGS. ENAMELS

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DEFECTS IN ALUMINUM COATINGS ON SILICATE GLASS

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Defects in fine aluminum coatings on silicate glasses are investigated using x-ray electron spectroscopy, secondary ionic mass-spectroscopy, and optical microscopy. The reasons for the emergence of defects are discussed.

The results of investigating the reasons for deterioration of the quality of aluminum mirrors produced by spray deposition on glass have been previously reported [1]. The chemical analysis of coatings was implemented using x-ray electron spectroscopy and secondary ion mass spectrometry. The x-ray electron spectra were excited by MgK_{α} radiation in an upgraded ÉS-2401 electron spectrometer. The vacuum level in the spectrometer chambers was 10^{-6} Pa. The purification of the surface from adsorbed air molecules was implemented by argon ionic bombardment with an energy of 0.9 keV. The study included the analysis of surface areas without defects and surface areas with various defects, both in the initial state and after pickling in alkaline solution.

The mirrors were produced by magnetron spraying of aluminum in an argon medium at a pressure of 10^{-5} Pa. The sprayed target (aluminum Ad0) is moving along the surface of the glass and represents the cathode in the used scheme, to which a negative potential of about 350 – 400 V is supplied. The second electrode is the case of the spraying chamber. The glass is fixed in insulation from the chamber case. The thickness of the coatings is 7 – 8 μm .

The initial glass had a composition of $SiO_2 \cdot CaO \cdot La_2O_3 \cdot Na_2O$ with the ratio of Si : Ca : La : Na equal to 76.1 : 14.7 : 7.9 : 1.4; in addition, a small quantity of Sb_2O_3 was added.

When spraying is implemented from a source in which the anode plates are arranged along the entire length of the aluminum cathode (i.e., a discharge occurs in the local space between the anode and the cathode) [1], the surface of the coating totally consists of aluminum (Table 1). The layer investigated in the present study, when the chamber case serves as the anode, in addition to aluminum contains a great quan-

tity of sodium, and some defects visible to the naked eye are observed in this layer. At the same time, the thin (10 – 15 nm) surface layer in defective spots contains half as much sodium as the area without defects.

The exposure of a defective sample in a KOH solution leads to dissolving of the major part of the aluminum coating. The layer analyzed by x-ray phase electron spectroscopy includes the glass – coating boundary region and the residue of the deposited layer. The sodium content in the investigated layer increases. The carbon analysis of the pure mirror area and the defective area pickled in alkaline indicated that the carbon content in the defective site is 1.5 – 2 times higher than in the mirror without defect.

As a result of mass-spectrometric analysis in the depth of the coating, it was found that the sodium content in the defective area is higher (5%) than in the bulk of the mirror without defect (not more than 1%). The amount of aluminum

TABLE 1

Sample	Component ratio, %*				
	Al	Ca	Si	Na	other elements
Glass without coating	–	14.4	76.1	1.4	7.9 La, 0.5 Sn
Mirror:					
1	89.6	1.8	–	–	2.6 S, 1.8 Cl, 1.1 F, 2.6 N
2	43.4	0.7	0.8	50.5	0.8 S, 0.8 F, 0.07 Cu
Defective area:					
initial	70.5	Traces	1.2	27.6	–
after pickling in KOH	41.6	3.3	4.1	40.0	4.1 S

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* Not taking into account oxygen and carbon (the thickness of the analyzed layer is 10 nm: thin surface layer).

oxides in the film and in the defective site is of approximately the same order (about 2%). The high sodium content in the thin surface layer of the coatings, as compared to their volume content in the film, is due to its segregation toward the surface. It is known that alkaline metals are prone to surface segregation.

Figure 1 exhibits typical defective areas in mirrors. The defect structure has a clearly expressed radial orientation. At least three types of defects are observed. Type-I defects in most cases exhibit a central fused or visually "undamaged" site and the surrounding relief extended on the surface, which resembles broken, crushed glass or marble crumbs with an evident texture directed from the center along the radius, whereas the density and the size of the microrelief details decrease towards the periphery. Type-II defects have an obvious circumferential delineation and a cross-sectional relief with symptoms of both fusion, especially at the edges, and evaporation of the material from the defective zone. The defects of type III have a clearly visible central fusion zone with a peripheral relief area, or else they are surrounded by a fused ring. Outside the defect boundary, it is possible to observe a thin circular trace around them, which is caused by the propagation of the thermal front from the defect center. The radial structure is evident in all types of defects.

The defects are optically more translucent, compared to the mirror without defects, which is due to their porosity, the presence of microcracks, and the smaller thickness of the deposited layer.

The structure of the defects gives reason to assume that they are the result of a local thermal effect (a thermomechanical shock) leading simultaneously to local fusion, evaporation of the film material from the surface, and mechanical cracking of surface sites. The reason for the thermomechanical destruction of the coating is the electric-spark shock and the local electric breakdown of the film. The electric-spark effect and the breakdown lead to local heating with the fusion of the middle part, and as the thermal front progresses from the center outwards, the destruction of the structure progresses towards the peripheral regions. The intense heating and the electric-spark effect cause vaporization and film erosion.

The defects are clearly divided into three classical types of breakdown in thin films: self-propagating breakdown (type I), local breakdown resembling drop spots (type II), and defects isolated by local fusion (type III) [2].

It should be noted that the large areas of self-propagating breakdown appear somewhat blurred in a certain direction. This can be related to the effect of a moving object.

The experiments with dissolving film in alkaline solutions indicated that the defective areas become pickled much sooner. This is due to their extended surface and the presence of pores and cracks. It was also found that film defects arise during the entire spraying process, whereas some sites of the coating are initially weaker. The early defects become healed by the coating at the later stages of spraying. Chemical pickling in some cases reveals an extended trace of an electric-

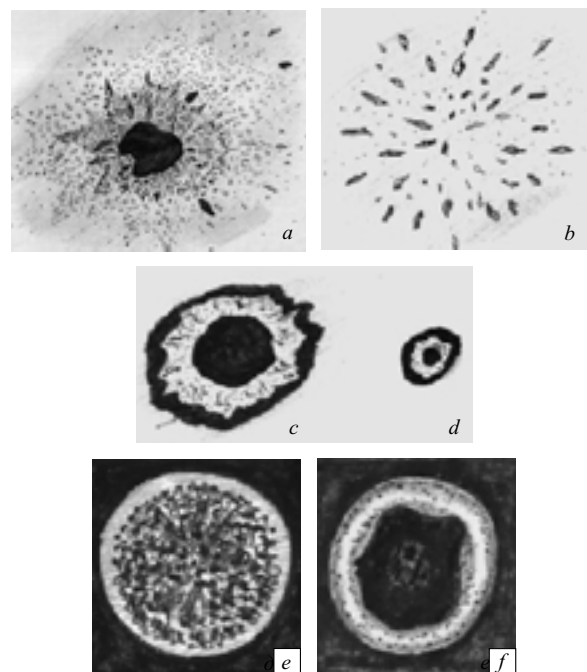


Fig. 1. Defects in aluminum coatings on silicate glass ($\times 50$): *a, b*) type-I defects; *c, d, e*) type-II defects; *f*) type-III defects.

spark breakdown near the main visible defect, which is several times longer than the defect itself, i.e., the breakdown had been creeping along the surface.

Some mirrors exhibit less frequent defects in the form of paths caused by a gliding spark discharge arising along the mirror surface. These paths are also easily pickled in alkali.

The mechanism of spark-discharge formation is known. The conditions required for this discharge to take place include the breakdown voltage, the presence of a sufficient quantity of charged particles (electrons, ions) in the gas space, and the existence of surface defects and sharp protruding structural parts. The conditions of breakdown in rarefied gas are substantially facilitated as soon as the length of the free electron run and the ion content increase. In this case, a voltage of a few hundred volts can be sufficient. The spraying chamber contains a fairly powerful source of electrons, namely, the heated aluminum target. The chemical analysis data indicate that the mirror surface (the thin surface layer) is rich in the alkaline element (sodium). The alkaline metals have the minimum values of electron-exit work, which contributes to the facile formation of an electric discharge in the space near the mirror.

The mechanism of electric breakdown in thin films is simple compared to massive materials. There are many reasons for a decrease in the breakdown field of thin films. The thin areas and polycrystalline borders can let through strong currents, which can be the reason for local fusions and thermomechanical destruction. A particular feature of the propagating breakdown is that it is observed even in relatively weak fields. The breakdown of types II and III occurs in the

weak points of the film, owing to the possible presence of dust and other inclusions on the surface of the substrate and inside the film.

The chemical analysis indicated that the carbon content in defective areas is 1.5 – 2 times higher than in pure mirror. The sodium content in these sites is higher as well (5% in defective areas against 1% in defect-free mirrors). The registered decrease in the sodium content in the thin surface layer of the defective areas, compared to defect-free areas, has the following explanation: thermal desorption of sodium from the thin surface layer occurs under strong local heating,

The thermal effects are determined by the increased strength of the current passing through these weak points. The maximum voltage of film breakdown varies, depending on the film thickness. The conditions for the emergence of

electric spark and breakdown in film can be facilitated by possible polarization of the substrate (glass).

Thus, the reason for the formation of defects in mirrors is the emergence of short-term electric discharges and electric breakdowns of the coating accompanied by local fusion, thermomechanical destruction, evaporation, and erosion of the coating material.

REFERENCES

1. V. I. Kozhevnikov, F. Z. Gil'mutdinov, and O. M. Kanunnikova, "The effect of the composition of residual atmosphere on the quality of aluminum mirrors," *Steklo Keram.*, No. 11, 15 – 17 (2000).
2. *Technology of Thin Films. A Reference Book, Vol. 2* [in Russian], Sovetskoe Radio, Moscow (1977).